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Description

The present invention is directed to a method for producing a microporous material characterized by both a very large proportion of finely divided particulat substantially water-insoluble siliceous filler and a very high void content.

GB-A-20 83 823 discloses a precursor microporous material which is a blend of a polyolefin such as a polymer of ethylene, propylene or butylene, finely divided silica and a di(C_{2-11}) alkyl phthalate or adipate as plasticizer. A sheet is formed and contacted with water for a time sufficient to render the sheet microporous.

From EP-A-193 318 a microporous membrane is known of ultrahigh molecular weight polypropylene with a void ratio of from 30 to 90 percent produced by forming a gel sheet from a solution of the polypropylene, removing a portion of the solvent, heating and stretching the sheet and removing the residual solvent.

Most often the microporous material is in the form of a thin sheet, film, or tube having a thickness across the microporous material in the range of from 0.03 to 0.25 millimeter, and in this form it exhibits high degrees of suppleness and softness to the touch which are surprisingly and wholly unexpected in view of the very large amount of inorganic filler present. It has the capacity to pass water vapor while resisting the transmission of liquid water and aqueous solutions, and hence it is suitable for use in, for example, breathable water proof garments, gloves, shoes, tents, and absorptive products such as wipers, diapers, incontinence devices, sanitary napkins and the like, where such properties are desirable. Even when the thickness of the microporous material is substantially greater than 0.25 millimeter, it has utility as a filter medium, substrate for protein immobilization, substrate for the slow release of medicaments or perfumes, and a multitude of other uses. In the thin form it is an especially useful material from which the petals of artificial flowers may be made. Such petals may optionally contain perfume and/or colorant when desired. The microporous material may be in a wide variety of other forms, including, by way of illustration, continuous fibers, non-continuous fibers, hollow fibers, and woven and non-woven fibrous mats.

It is the object of the present invention to provide a method for preparing a microporous material having a high void content.

This object is attained by

a method for producing a microporous material by

(a) forming a sheet from a mixture comprising

(i) essentially linear ultrahigh molecular weight polyethylene having an intrinsic viscosity of at least 18 deciliters/gram, or essentially linear ultrahigh molecular weight polypropylene having an intrinsic viscosity of at least 6 deciliters/gram or a mixture thereof

(ii) finely divided particulate substantially water-insoluble siliceous filler, wherein the weight ratio of said filler to polymer being in the range of from 1:1 to 9:1 and

(iii) processing plasticizer which is liquid at room temperature and having little solvating effect on the polymer,

(b) removing said processing plasticizer from said sheet resulting in precursor microporous material having

(1) a matrix consisting of said essentially ultrahigh molecular weight polyolefin,

(2) finally divided particulate substantially water-insoluble siliceous filler distributed throughout the matrix, said filler constituting from 50 percent to 90 percent by weight of said precursor microporous material and

(3) a network of interconnecting pores communicating throughout said precursor microporous material, said pores constituting from 35 percent to 80 percent by volume of said precursor microporous material

characterized by

(c) stretching said precursor microporous material in at least one stretching direction to a stretch ratio of at least 1,5 to produce a stretched microporous material which is dimensionally stable at room temperature and comprising regions of stretched-induced molecularly orientated ultrahigh molecular weight polyolefin and wherein the network of interconnecting pores communicating throughout said stretched microporous material constituting more than 80 percent by volume of said stretched microporous material.

Preferably the mixtru is extruded to a continuous sheet and calendered to form a continuous sheet of lesser thickness than the sheet existing from th extrusion di .

A preferred method of the invention is characterized by

(i) substantially removing the processing plasticizer by extraction with an organic liquid which is a good solvent for the processing plasticizer, a poor solvent for the polymer and more volatile than the

processing plasticizer,

(ii) substantially removing the organic extraction liquid by steam and/or water, and

(iii) drying th precursor microporous material prior stretching to remove th residual wat r and remaining residual organic extraction liquid.

It will be appreciated from the above that the stretching both increases the void volume of the material and induces regions of molecular orientation in the ultrahigh molecular weight (UHMW) polyolefin. As is well known in the art, many of the physical properties of molecularly oriented thermoplastic organic polymer, including tensile strength, tensile modulus, Young's modulus, and others, differ considerably from those of the corresponding thermoplastic organic polymer having little or no molecular orientation. Although it is not desired to be bound by any theory, it is believed that the properties of the UHMW polyolefin, the regions of molecular orientation, the high levels of filler loading, and the high degrees of porosity cooperate to provide many of the desirable properties characteristic of the microporous material of the invention.

The microporous material is non-isotropic, that is, the pore or microvoid shapes and distributions of pore or microvoid sizes are not the same in planes perpendicular to the surface as in planes parallel to the surface.

Inasmuch as UHMW polyolefin is not a thermoset polymer having an infinite molecular weight, it is technically classified as a thermoplastic. However, because the molecules are essentially very long chains, UHMW polyolefin, and especially UHMW polyethylene, softens when heated but does not flow as a molten liquid in a normal thermoplastic manner. The very long chains and the peculiar properties they provide to UHMW polyolefin are believed to contribute in large measure to the desirable properties of the microporous material.

As indicated earlier, the intrinsic viscosity of the UHMW polyethylene is at least 18 deciliters/gram. In many cases the intrinsic viscosity is at least 19 deciliters/gram. Although there is no particular restriction on the upper limit of the intrinsic viscosity, the intrinsic viscosity is frequently in the range of from 18 to 39 deciliters/gram. An intrinsic viscosity in the range of from 18 to 32 deciliters/gram is preferred.

Also as indicated earlier the intrinsic viscosity of the UHMW polypropylene is at least 6 deciliters/gram. In many cases the intrinsic viscosity is at least 7 deciliters/gram. Although there is no particular restriction on the upper limit of the intrinsic viscosity, the intrinsic viscosity is often in the range of from 6 to 18 deciliters/gram. An intrinsic viscosity in the range of from 7 to 16 deciliters/gram is preferred.

As used herein and in the claims, intrinsic viscosity is determined by extrapolating to zero concentration the reduced viscosities or the inherent viscosities of several dilute solutions of the UHMW polyolefin where the solvent is freshly distilled decahydronaphthalene to which 0.2 percent by weight, 3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid, neopentanetetrayl ester [CAS Registry No. 6683-19-8] has been added. The reduced viscosities or the inherent viscosities of the UHMW polyolefin are ascertained from relative viscosities obtained at 135 °C. using an Ubbelohde No. 1 viscometer in accordance with the general procedures of ASTM D 4020-81, except that several dilute solutions of differing concentration are employed.

The nominal molecular weight of UHMW polyethylene is empirically related to the intrinsic viscosity of the polymer according to the equation:

$$M = 5.37 \times 10^4 [\eta]^{1.37}$$

where M is the nominal molecular weight and $[\eta]$ is the intrinsic viscosity of the UHMW polyethylene expressed in deciliters/gram. Similarly, the nominal molecular weight of UHMW polypropylene is empirically related to the intrinsic viscosity of the polymer according to the equation:

$$M = 8.88 \times 10^4 [\eta]^{1.25}$$

where M is the nominal molecular weight and $[\eta]$ is the intrinsic viscosity of the UHMW polypropylene expressed in deciliters/gram.

The essentially linear ultrahigh molecular weight polypropylene is most frequently essentially linear ultrahigh molecular weight isotactic polypropylene. Often the degree of isotacticity of such polymer is at least 95 percent, while preferably it is at least 98 percent.

Sufficient UHMW polyolefin should be present in the matrix to provide its properties to the microporous mat rial. Other thermoplastic organic polymer may also be present in the matrix so long as its pr sence does not materially affect the properties of the microporous material in an advers mann r. Th amount of the other thermoplastic polymer which may be present depends upon the nature of such polymer. In general, a greater amount of other thermoplastic organic polymer may be used if the molecular structure contains little branching, few long sidechains, and few bulky side groups, than when there is a large amount

of branching, many long sidechains, or many bulky side groups. For this reason, the preferred thermoplastic organic polymers which may optionally b present are low density polyethylene, high density polyethylene, poly(tetrafluoroethylene), polypropylene, copolymers of ethyl n and propylen , copolymers of ethylene and acrylic acid, and copolymers of ethylene and methacrylic acid. If desired, all or a portion of the carboxyl groups of carboxyl-containing copolymers may be neutralized with sodium, zinc or the like. It is our experience that usually at least about 70 percent UHMW polyolefin, based on the weight of the matrix, will provide the desired properties to the microporous material. In most cases, however, it is preferred that the other thermoplastic organic polymer be substantially absent.

The finely divided substantially water-insoluble siliceous filler used in the present invention is particulate. As present in the microporous material, the filler may be in the form of ultimate particles, aggregates of ultimate particles, or a combination of both. In most cases, at least about 90 percent by weight of the filler used in preparing the microporous material has gross particle sizes in the range of from 5 to 40 micrometers as determined by use of a Model TAII Coulter counter (Coulter Electronics, Inc.) according to ASTM C 690-80 but modified by stirring the filler for 10 minutes in Isoton® II electrolyte (Curtin Matheson Scientific, Inc.) using a four-blade, 4.445 centimeter diameter propeller stirrer. Preferably at least about 90 percent by weight of the filler has gross particle sizes in the range of from 10 to 30 micrometers. It is expected that the sizes of filler agglomerates will be reduced during processing of the ingredients to prepare the microporous material. Accordingly, the distribution of gross particle sizes in the microporous material may be smaller than in the raw filler itself.

Examples of suitable siliceous fillers include silica, mica, montmorillonite, kaolinite, asbestos, talc, diatomaceous earth, vermiculite, natural and synthetic zeolites, cement, calcium silicate, aluminum silicate, sodium aluminum silicate, aluminum polysilicate, alumina silica gels, and glass particles. In addition to the siliceous fillers other finely divided particulate substantially water-insoluble fillers may also be employed. Examples of such optional fillers include carbon black, charcoal, graphite, titanium oxide, iron oxide, copper oxide, zinc oxide, antimony oxide, zirconia, mangnesia, alumina, molybdenum disulfide, zinc sulfide, barium sulfate, strontium sulfate, calcium carbonate, and magnesium carbonate.

Silica and the clays are the preferred siliceous fillers. Of the silicas, precipitated silica, silica gel, or fumed silica is most often used.

The particularly preferred finely divided particulate substantially water-insoluble siliceous filler is precipitated silica. Although both are silicas, it is important to distinguish precipitated silica from silica gel inasmuch as these different materials have different properties. Reference in this regard is made to R. K. Iler, The Chemistry of Silica, John Wiley & Sons, New York (1979), Library of Congress Catalog No. QD 181.S6144. Note especially pages 15-29, 172-176, 218-233, 364-365, 462-465, 554-564, and 578-579. Silica gel is usually produced commercially at low pH by acidifying an aqueous solution of a soluble metal silicate, typically sodium silicate, with acid. The acid employed is generally a strong mineral acid such as sulfuric acid or hydrochloric acid although carbon dioxide is sometimes used. Inasmuch as there is essentially no difference in density between gel phase and the surrounding liquid phase while the viscosity is low, the gel phase does not settle out, that is to say, it does not precipitate. Silica gel, then, may be described as a nonprecipitated, coherent, rigid, three-dimensional network of contiguous particles of colloidal amorphous silica. The state of subdivision ranges from large, solid masses to submicroscopic particles, and the degree of hydration from almost anhydrous silica to soft gelatinous masses containing on the order of 100 parts of water per part of silica by weight, although the highly hydrated forms are only rarely used in the present invention.

Precipitated silica is usually produced commercially by combining an aqueous solution of a soluble metal silicate, ordinarily alkali metal silicate such as sodium silicate, and an acid so that colloidal particles will grow in weakly alkaline solution and be coagulated by the alkali metal ions of the resulting soluble alkali metal salt. Various acids may be used, including the mineral acids, but the preferred acid is carbon dioxide. In the absence of a coagulant, silica is not precipitated from solution at any pH. The coagulant used to effect precipitation may be the soluble alkali metal salt produced during formation of the colloidal silica particles, it may be added electrolyte such as a soluble inorganic or organic salt, or it may be a combination of both.

Precipitated silica, then, may be described as precipitated aggregates of ultimate particles of colloidal amorphous silica that have not at any point xisted as macroscopic g l during the preparation. The sizes of the aggregates and the degree of hydration may vary widely.

Precipitated silica powders differ from silica gels that have been pulverized in ordinarily having a more open structure, that is, a higher specific por volume. However, the specific surface area of precipitated silica as measured by the Brunauer, Emmett, Teller (BET) method using nitrogen as th adsorbate, is often lower than that of silica g l.

Many different precipitated silicas may be employed in the present invention, but the preferred precipitated silicas are those obtained by precipitation from an aqueous solution of sodium silicate using a suitable acid such as sulfuric acid, hydrochloric acid, or carbon dioxide. Such precipitated silicas are themselves known and proc sses for producing them are described in detail in US-A-2,940,830 and in DE-A-35 45 615, including especially the processes for making precipitated silicas and the properties of the products.

In the case of the preferred filler, precipitated silica, the average ultimate particle size (irrespective of whether or not the ultimate particles are agglomerated) is less than 0.1 micrometer as determined by transmission electron microscopy. Often the average ultimate particle size is less than 0.05 micrometer. Preferably the average ultimate particle size of the precipitated silica is less than 0.03 micrometer.

The finely divided particulate substantially water-insoluble siliceous filler constitute from 50 to 90 percent by weight of the microporous material. Frequently such filler constitutes from 50 percent to 85 percent by weight of the microporous material. From 60 percent to 80 percent by weight is preferred.

Minor amounts, usually less than about 5 percent by weight, of other materials used in processing such as lubricant, plasticizer, processing plasticizer, organic extraction liquid, surfactant, water, and the like, may optionally also be present. Yet other materials introduced for particular purposes may optionally be present in the microporous material in small amounts, usually less than about 15 percent by weight. Examples of such materials include antioxidants, ultraviolet light absorbers, flame retardants, reinforcing fibers such as chopped glass fiber strand, dyes, pigments, and the like. The balance of the microporous material, exclusive of filler and any impregnant applied for one or more special purposes, is essentially the thermoplastic organic polymer.

On an impregnant-free basis, pores constitute more than 80 percent by volume of the microporous material. In many instances the pores constitute at least 85 percent by volume of the microporous material. Often the pores constitute from more than 80 percent to 95 percent by volume of the microporous material. From 85 percent to 95 percent by volume is preferred. As used herein and in the claims, the porosity (also known as void volume) of the microporous material, expressed as percent by volume, is determined according to the equation:

$$\text{Porosity} = 100[1-d_1/d_2]$$

where d_1 is the density of the sample which is determined from the sample weight and the sample volume as ascertained from measurements of the sample dimensions and d_2 is the density of the solid portion of the sample which is determined from the sample weight and the volume of the solid portion of the sample. The volume of the solid portion of the sample is determined using a Quantachrome stereopycnometer (Quantachrome Corp.) in accordance with the accompanying operating manual.

The volume average diameter of the pores of the microporous sheet is determined by mercury porosimetry using an Autoscan mercury porosimeter (Quantachrome Corp.) in accordance with the accompanying operating manual. The volume average pore radius for a single scan is automatically determined by the porosimeter. In operating the porosimeter, a scan is made in the high pressure range (from 138 kilopascals absolute to 227 megapascals absolute). If about 2 percent or less of the total intruded volume occurs at the low end (from 138 to 250 kilopascals absolute) of the high pressure range, the volume average pore diameter is taken as twice the volume average pore radius determined by the porosimeter. Otherwise, an additional scan is made in the low pressure range (from 7 to 165 kilopascals absolute) and the volume average pore diameter is calculated according to the equation:

$$d = 2\left(\frac{v_1 r_1}{w_1} \quad \frac{v_2 r_2}{w_2}\right) \Big/ \left(\frac{v_1}{w_1} \quad \frac{v_2}{w_2}\right)$$

where d is the volume average pore diameter, v_1 is the total volume of mercury intruded in the high pressure range, v_2 is the total volume of mercury intruded in the low pressur range, r_1 is the volume average pore radius determined from the high pressure scan, r_2 is the volume averag pore radius determined from th low pressur scan, w_1 is th weight of the sample subjected to the high pressure scan, and w_2 is the weight of the sample subjected to the low pr ssure scan. Gen rally the volume average diameter of the pores is in the range of from 0.6 to 50 micrometers. Very often the volum average diam t r of the pores is in the range of from 1 to 40 micrometers. From 2 to 30 micrometers is preferred.

In the course of determining the volume averag pore diameter by the above procedure, th maximum pore radius detected is som times noted. This is taken from the low pressure range scan if run; oth rwise it is taken from the high pressure range scan. The maximum pore diameter is twice the maximum pore radius.

The microporous sheet of the invention may be produced by stretching precursor microporous material according to the method of the invention.

The precursor microporous material may be produced according to the general principles and procedures of US-A-3,351,495, including especially the processes for making microporous materials and the properties of the products.

Preferably filler, thermoplastic organic polymer powder, processing plasticizer and minor amounts of lubricant and antioxidant are mixed until a substantially uniform mixture is obtained. The weight ratio of filler to polymer powder employed in forming the mixture is essentially the same as that of the precursor microporous material and that of the stretched microporous material to be produced. The mixture, together with additional processing plasticizer, is introduced to the heated barrel of a screw extruder. Attached to the extruder is a sheeting die. A continuous sheet formed by the die is forwarded without drawing to a pair of heated calender rolls acting cooperatively to form continuous sheet of lesser thickness than the continuous sheet exiting from the die. The continuous sheet from the calender then passes to a first extraction zone where the processing plasticizer is substantially removed by extraction with an organic liquid which is a good solvent for the processing plasticizer, a poor solvent for the organic polymer, and more volatile than the processing plasticizer. Usually, but not necessarily, both the processing plasticizer and the organic extraction liquid are substantially immiscible with water. The continuous sheet then passes to a second extraction zone where the residual organic extraction liquid is substantially removed by steam and/or water. The continuous sheet is then passed through a forced air dryer for substantial removal of residual water and remaining residual organic extraction liquid. From the dryer the continuous sheet, which is precursor microporous material, is passed to a take-up roll.

The processing plasticizer has little solvating effect on the thermoplastic organic polymer at 60°C, only a moderate solvating effect at elevated temperatures on the order of about 100°C, and a significant solvating effect at elevated temperatures on the order of about 200°C. It is a liquid at room temperature and usually it is processing oil such as paraffinic oil, naphthenic oil, or an aromatic oil. Suitable processing oils include those meeting the requirements of ASTM D 2226-82, Types 103 and 104. Preferred are those oils which have a pour point of less than 22°C according to ASTM D 97-66 (reapproved 1978). Particularly preferred are oils having a pour point of less than 10°C. Examples of suitable oils include Shellflex® 412 and Shellflex® 371 oil (Shell Oil Co.) which are solvent refined and hydrotreated oils derived from naphthenic crude. It is expected that other materials, including the phthalate ester plasticizers such as dibutyl phthalate, bis(2-ethylhexyl) phthalate, diisodecyl phthalate, dicyclohexyl phthalate, butyl benzyl phthalate, and ditridecyl phthalate, will function satisfactorily as processing plasticizers.

There are many organic extraction liquids that can be used. Examples of suitable organic extraction liquids include 1,1,2-trichloroethylene, perchloroethylene, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, methylene chloride, chloroform, isopropyl alcohol, diethyl ether and acetone.

In the above described process for producing precursor microporous material, extrusion and calendering are facilitated when the substantially water-insoluble filler carries much of the processing plasticizer. The capacity of the filler particles to absorb and hold the processing plasticizer is a function of the surface area of the filler. It is therefore preferred that the filler have a high surface area. High surface area fillers are materials of very small particle size, materials having a high degree of porosity or materials exhibiting both characteristics. Usually the surface area of the filler itself is in the range of from 20 to 400 square meters per gram as determined by the Brunauer, Emmett, Teller (BET) method according to ASTM C 819-77 using nitrogen as the adsorbate but modified by outgassing the system and the sample for one hour at 130°C. Preferably the surface area is in the range of from 25 to 350 square meters per gram.

Inasmuch as it is desirable to essentially retain the filler in the precursor microporous sheet, it is preferred that the substantially water-insoluble filler be substantially insoluble in the processing plasticizer and substantially insoluble in the organic extraction liquid when precursor microporous material is produced by the above process.

The precursor microporous material comprises finely divided substantially water-insoluble siliceous filler, th rmoplastic organic polymer which consists essentially of the UHMW polyol fin, and optional materials in essentially the same weight proportions as those discussed above in respect of th stretched sheet. The r sidual processing plasticiz r content is usually less than 5 perc nt by weight of the precursor microporous sheet and this may be reduced even further by additional extractions using the same or a different organic extraction liquid.

Pores constitut from 35 to 80 percent by volume of the precursor microporous material. In many cases the pores constitute from 60 to 75 perc nt by volume of the precursor microporous material. The porosity of the precursor microporous material, expressed as p rc nt by volume, is determined by th same procedur described above in respect of the stretched microporous material. In all cases, the porosity of the microporous material is, unless impregnated after stretching, greater than that of the precursor microporous material.

The volume average diameter of the pores of the precursor microporous material as determined by the mercury porosimetry method previously described in respect of the stretched microporous material, is usually in the range of from 0.02 to 0.5 micrometers. Frequently the average diameter of the pores is in the range of from 0.04 to 0.3 micrometers. From 0.05 to 0.25 micrometers is preferred.

The microporous material is produced by stretching the precursor microporous material in at least one stretching direction to a stretch ratio of at least 1.5. In many cases the stretch ratio is at least 1.7. Preferably it is at least 2. Frequently the stretch ratio is in the range of from 1.5 to 15. Often the stretch ratio is in the range of from 1.7 to 10. Preferably the stretch ratio is in the range of from 2 to 6. As used herein and in the claims, the stretch ratio is determined by the formula:

$$S = L_2/L_1$$

where S is the stretch ratio, L_1 is the distance between two reference points located on the precursor microporous material and on a line parallel to the stretching direction, and L_2 is the distance between the same two reference points located on the stretched microporous material.

The temperatures at which stretching is accomplished may vary widely. In most cases, the stretching temperatures are in the range of from 20 °C to 450 °C. Often such temperatures are in the range of from 50 °C to 400 °C. From 100 °C to 375 °C is preferred.

Stretching may be accomplished in a single step or a plurality of steps as desired. For example, when the precursor microporous material is to be stretched in a single direction (uniaxial stretching), the stretching may be accomplished by a single stretching step or a sequence of stretching steps until the desired final stretch ratio is attained. Similarly, when the precursor microporous material is to be stretched in two directions (biaxial stretching), the stretching can be conducted by a single biaxial stretching step or a sequence of biaxial stretching steps until the desired final stretch ratios are attained. Biaxial stretching may also be accomplished by a sequence of one or more uniaxial stretching steps in one direction and one or more uniaxial stretching steps in another direction. Biaxial stretching steps where the precursor microporous material is stretched simultaneously in two directions and uniaxial stretching steps may be conducted in sequence in any order. Stretching in more than two directions is within contemplation. It may be seen that the various permutations of steps are quite numerous. Other steps, such as cooling, heating, sintering, annealing, reeling, unreeling, and the like, may optionally be included in the overall process as desired.

Various types of stretching apparatus are well known and may be used to accomplish stretching of the precursor microporous material according to the present invention. Uniaxial stretching is usually accomplished by stretching between two rollers wherein the second or downstream roller rotates at a greater peripheral speed than the first or upstream roller. Uniaxial stretching can also be accomplished on a standard tentering machine. Biaxial stretching may be accomplished by simultaneously stretching in two different directions on a tentering machine. More commonly, however, biaxial stretching is accomplished by first uniaxially stretching between two differentially rotating rollers as described above, followed by either uniaxially stretching in a different direction using a tenter machine or by biaxially stretching using a tenter machine. The most common type of biaxial stretching is where the two stretching directions are approximately at right angles to each other. In most cases where continuous sheet is being stretched, one stretching direction is at least approximately parallel to the long axis of the sheet (machine direction) and the other stretching direction is at least approximately perpendicular to the machine direction and is in the plane of the sheet (transverse direction).

After stretching has been accomplished, the microporous material may optionally be sintered, annealed, heat set and/or otherwise heat treated. During these optional steps, the stretched microporous material is usually held under tension so that it will not markedly shrink at the elevated temperatures employed, although som relaxation amounting to a small fraction of the maximum stretch ratio is fr quently permitted.

Following stretching and any heat treatments employed, tension is released from the stretched microporous material aft r th microporous material has been brought to a temperature at which, except for a small amount of elastic recovery amounting to a small fraction of th stretch rati , it is ssentially dimensionally stable in the absence of tension. Elastic recovery under these conditions usually do s not amount to more than 10 percent of the stretch ratio.

The stretched microporous material may then be further processed as d sired. Examples of such further processing steps include reeling, cutting, stacking, treatment to remove residual processing plasticizer or extraction solvent, impregnation with various materials, fabrication into shapes for various end uses, and lamination to one of more backings of reinforcing fibers such as woven fabrics, knitted fabrics, or mats. The preferred reinforcing fibers are glass fibers, particularly in the form of glass fiber cloth or glass fiber mat.

The invention is further described in conjunction with the following examples which are to be considered illustrative rather than limiting.

EXAMPLES

Precursor Sheet Formation

The preparation of the above described materials is illustrated by the following descriptive examples. Processing oil was used as the processing plasticizer. Silica, polymer, lubricant and antioxidant in the amounts specified in Table I were placed in a high intensity mixer and mixed at high speed for 30 seconds to thoroughly blend the dry ingredients. The processing oil needed to formulate the batch was pumped into the mixer over a period of 2-3 minutes with low speed agitation. After the completion of the processing oil addition a 2 minute low speed mix period was used to distribute the processing oil uniformly throughout the mixture.

Table I

Formulations			
Example	1	2	3
Ingredient			
UHMWPE (1), kg	5.67	9.98	4.25
Polypropylene (2), kg	0	0	1.42
Silica (3), kg	19.96	19.96	19.96
Lubricants (4), g	100	100	100
Antioxidant (5), g	100	100	100
Processing Oil (6), kg			
in Batch	31.21	31.21	31.21
at Extruder	13.61	41.59	30.39

(1) UHMWPE = Ultrahigh Molecular Weight Polyethylene, Himont® 1900, Himont, U.S.A., Inc.
(2) Profax® 6801, Himont U.S.A., Inc.
(3) HiSil® SBG, PPG Industries, Inc.
(4) Petrac® CZ81, Desoto, Inc., Chemical Speciality Division
(5) Irganox® B-215, Ciba-Geigy Corp.
(6) Shellflex® 412, Shell Chemical Co.

The batch was then conveyed to a ribbon blender where it was mixed with up to two additional batches of the same composition. Material was fed from the ribbon blender to a twin screw extruder by a variable rate screw feeder. Additional processing oil was added via a metering pump into the feed throat of the extruder. The extruder mixed and melted the formulation and extruded it through a 76.2 centimeter x 0.3175 centimeter slot die. The extruded sheet was then calendered. The hot, calendered sheet was then passed around a chill roll to cool the sheet. The rough edges of the cooled calendered sheet were trimmed by rotary knives to the desired width.

The oil filled sheet was conveyed to th extractor unit where it was contacted by both liquid and vaporized 1,1,2-trichloroethylen (TCE). The sheet was transported over a series of rollers in a serpentine fashion to provide multiple, sequential vapor/liquid/vapor contacts. The extraction liquid in the sump was maintained at a temperature of 65-88°C. Overflow from the sump of the TCE extractor was returned to a still which recovered the TCE and th processing oil for reuse in the process. Th bulk of the TCE was extracted from the sheet by steam as the sheet was pass d through a second extractor unit. A description

of these types of extractors may be found in EP-A-191 615, including especially the structures of the devices and th ir mod s of op ration. The sheet was dried by radiant heat and convectiv air flow. The dried sheet was wound on cores to provide roll stock for further processing.

Th three precursor microporous sheets, as well as the hereinafter described biaxially stretched microporous sheets produced therefrom, were tested for various physical properties. Table II identifies the properties with the methods used for their determination. The various ASTM and TAPPI test methods and Method 502 C are referenced in Table II. The results of physical testing of the three precursor microporous sheets are shown in Table III.

Property values indicated by MD (machine direction) were obtained on samples whose major axis was oriented along the length of the sheet. TD (transverse direction; cross machine direction) properties were obtained from samples whose major axis was oriented across the sheet.

Table II

Physical Test Methods	
Property	**Test Method**
Tensile Strength Elongation	ASTM D 412-83.
Porosity	As described in the text above.
Matrix Tensile Strength	Tensile Strength determined in accordance with ASTM D 412-83 multiplied by the quantity 100/(100-Porosity).
Tear Strength, Die C	ASTM D 624-81.
Processing Oil Content	Method 502 C in "Standard Methods for the Examination of Water and Wastewater", 14th Ed., APHA-AWWA-WPCF (1975).
Maximum Pore Diameter	Mercury Porosimetry, as described in the text above.
Volume Average Pore Diameter	Mercury Porosimetry, as described in the text above.
Gurley Air Flow	ASTM D 726-58 (reapproved 1971), Method A.
Opacity	TAPPI Standard T 425 (Contrast Ratio) using Illuminant C instead of Illuminant A.
Brightness	TAPPI Standard T 452.
Mullens Hydrostatic Resistance	ASTM D 751-79, Sec. 30-34, Method A.
MVTR (Moisture Vapor Transmission Rate)	ASTM E 96-80.
Methanol Bubble Pressure	ASTM F 316-80, using methanol.
Maximum Limiting Pore Diameter	ASTM F-316-80, using methanol where c_γ = 22.34 (µ m)(kPa).
Heat Shrinkage	ASTM D 1204-84, using 15.24 cm x 20.32 cm sample, 1 hr at 100 °C.

Table III

Physical Properties of Precursor Microporous Sheet			
Example	1	2	3
Thickness, mm	0.229	0.279	0.229
Matrix Tensile Strength, MPa			
MD	23.82	34.33	25.66
TD	9.94	14.91	10.38
Elongation at Break, %			
MD	250	279	227
TD	108	140	112
Tear Strength, kN/m			
MD	36.25	61.47	47.81
TD	18.04	39.93	23.12
Porosity, vol%	71	66	68
Processing Oil Content, wt %	4.1	2.7	2.4
Maximum Pore Diameter, µm	0.86	0.30	0.28
Volume Average Pore Diameter, µm	0.11	0.065	0.069
Gurley Air Flow, sec/100cc	904		955
Opacity, %	96.0	95.1	94.4
Brightness, %	87.8	92.6	92.0

Biaxial Stretching of Precursor Microporous Sheet

The precursor materials produced in Examples 1-3 were unwound from cores and biaxially stretched by first uniaxially stretching in the machine direction using a single stage roll-to-roll machine direction stretching (MDS) unit and then essentially uniaxially stretching in the transverse direction using a moving clip tenter frame as a transverse direction stretching (TDS) unit. A preheat roll was employed with the MDS unit to heat the sheet prior to stretching. In the TDS unit, the sheet was heated by infrared radiant heaters and the temperature was controlled in banks to provide a temperature profile along the length of the sheet and substantially constant film temperature across the sheet at any point. For a description of a typical TDS unit, see Figure 2 and column 2, lines 43-69, of US-A-2,823,421. The MDS stretch ratio was varied by controlling the relative peripheral speeds of the feed rolls and the takeoff rolls of the MDS unit. The chain track positions in the tenter frame were set to achieve the desired stretch ratio and then to essentially maintain that stretch ratio during sintering. For each of Examples 4-25, the settings of one of the last four vertical columns in Table IV were employed. The correct column may be ascertained by matching up the TD stretch ratio of the example with the final stretch ratio of the column.

Table IV

Transverse Direction Stretching

Zone	Cumulative Length Along Tenter Frame Track, meters	Transverse Stretch Ratio			
Preheat	0	1	1	1	1
Stretch I	3.048	1	1	1	1
Stretch II	6.858	1.25	1.5	2	2.5
Sinter I	10.668	2.5	3	4	5
Sinter II	13.716	2.5	3	4	5
	16.764	2.5	3	4	5

The precursor sheet stock of Examples 1-3 was fed over the preheat roll of the MDS unit which was heated to the temperature indicated in Tables V-VII. The sheet was then stretched to the indicated stretch ratio by maintaining the relative peripheral speeds of the second and first stretch rolls at essentially the same ratio as the stretch ratio. The line speed given in Tables V-VII is the output speed of the MDS unit and the machine direction speed of the TDS unit. The linear feed rate from the roll stock of precursor microporous material to the MDS unit was set at a value given by the line speed divided by the MDS stretch ratio. Thus, with a line speed of 24 m/min and a MDS stretch ratio of 2, the linear feed rate from the roll stock to the MDS unit would be 12 m/min. The properties of several representative examples of biaxially stretched sheets are given in Tables V-VII.

Table V
Properties of Biaxially Stretched Microporous Sheets Produced from Precursor Sheet of Example 1

Example No.	4	5	6	7	8	9	10	11	12
Thickness, mm	0.178	0.152	0.127	0.076	0.076	0.102		0.102	0.076
Stretch Ratio									
MD	2	2	2	2	3	3	3	3	3
TD	3	3	4	5	3	3	3	3	4
Line Speed m/min	48.8	24.4	24.4	24.4	24.4	24.4	24.4	24.4	24.4
MDS Preheat Temp., °C	79	79	79	79	79	79	79	79	79
TDS Zone Temp, °C									
Preheat	149	177	177	149	149	149	177	149	177
Stretch I									
177-166-177							X		X
193-182-18		X	X						
193-185-193	X			X	X	X		X	
Stretch II, Sinter I									
149-127-149		X	X				X		X
149-149-149	X			X	X	X		X	
Sinter II									
149-149-149					X				
204-204-204	X			X		X			
232-204-232		X	X				X		X
260-260-260								X	
Weight, g/m^2	27	24	17	14	14	10	14	14	10
Porosity, vol%	91	90	92	90	89	93	93	93	91
Matrix Tensile Strength, MPa									
MD	53.70	32.96	40.25	25.30	29.52	62.74	67.77	41.96	56.69
TD	40.14	29.30	65.76	46.54	61.99	45.41	43.93	57.62	55.77
Elongation at break, %									
MD	57	56	60	67	26	23	34	18	33
TD	27	41	13	9	23	27	30	31	12

Table V (continued)
Properties of Biaxially Stretched Microporous Sheets
Produced from Precursor Sheet of Example 1

Example No.	4	5	6	7	8	9	10	11	12
Tear Strength, kN/m									
MD	9.28	5.78	7.01	3.85	2.28	5.08	6.30	5.60	5.08
TD	4.90	4.90	7.01	8.23	7.53	1.93	4.38	4.55	4.73
Gurley Air Flow, sec/100cc	47	45	40	29	32	28	37	28	36
Mullens Hydrostatic, kPa	483	434	490	448	476	503	496	434	510
MVTR, g/m^{2}day	935						878	963	
Methanol Bubble Point Pressure, kPa	290	276	296	234	145	276		55	317
Maximum Limiting Pore Diameter, μm	0.077	0.081	0.075	0.095	0.154	0.081		0.406	0.070
Maximum Pore Diameter, μm							155		
Volume Average Pore Diameter, μm									
Heat Shrinkage after 1 hr at 100°C., %									
MD	19.0		9.4	12.0		19.3	24.1	21.2	
TD	23.2		22.5	28.3		25.7	29.1	30.8	

The biaxially stretched microporous sheet of Example 10 was examined by scanning electron microscopy at a magnification of 430X. A section taken in a plane perpendicular to the sheet surface (viz., looking into the thickness) and along the machine direction showed substantial pore elongation. A section taken in a plane perpendicular to the sheet surface and along the transverse direction showed pore elongation which was not as pronounced as along the machine direction. A view of the sheet surface (not sectioned) showed that large void structures were not as numerous as in views of either of the sections looking into the thickness.

Table VI
Properties of Biaxially Stretched Microporous Materials
Produced from Precursor Sheet of Example 2

Example No.	13	14	15	16	17	18	19	20	21
Thickness, mm	0.203	0.152	0.191	0.140	0.152	0.152	0.102	0.114	0.203
Stretch Ratio									
MD	2	2	2	2	2	3	3	3	3
TD	2.5	3	3	3	4	3	3	3	4
Line Speed m/min	24.4	24.4	24.4	24.4	15.2	24.4	24.4	24.4	15.2
MDS Preheat Temp., °C	104	104	121	79	121	104	121	79	121
TDS Zone									
Temp., °C									
Preheat	177	177	149	149	149	177	149	149	149
Stretch I									
177-166-177	X	X				X			
193-182-193			X	X	X		X	X	X
Stretch II									
149-127-149	X	X				X			
149-149-149				X			X		
149-135-149			X		X			X	X
Sinter I									
149-127-149	X	X				X			
149-149-149				X			X		
149-135-149					X				X
204-191-204			X					X	
Sinter II									
232-204-232	X	X				X			
260-246-260			X		X		X		X
316-316-316				X				X	
Weight, g/m^2	44	24			24	17			31
Porosity, vol%	86	90			90	92			90
Matrix Tensile Strength, MPa									
MD	52.94	61.50			36.61	96.18			37.23
TD	44.47	67.98			109.54	54.39			117.21

Table VI (continued)
Properties of Biaxially Stretched Microporous Materials
Produced from Precursor Sheet of Example 2

Example No.	13	14	15	16	17	18	19	20	21
Elongation at Break, %									
MD	58	54	25	41	87	31	13	19	111
TD	51	39	15	16	9	42	16	16	7
Tear Strength, kN/m									
MD	20.31	12.61	17.51	6.13	13.13	12.26	8.41	5.95	18.56
TD	13.31	12.78	21.02	7.18	11.03	9.11	5.25	7.53	19.44
Gurley Air Flow, sec/100cc	81	40			46	45			52
Mullens Hydrostatic, kPa	745	689	676	496	745	717	641	503	703
MVTR, g/m^2day			868	761		947	913	827	
Methanol Bubble Point Pressure, kPa	290	303			303	365			290
Maximum Limiting Pore Diameter, μm	0.077	0.074			0.074	0.061			0.077
Maximum Pore Diameter, μm		111				> 146			
Volume Average Pore Diameter, μm		7.13				4.70			
Heat Shrinkage after 1 hr at 100°C., %									
MD	11.7		3.8	7.1	12.3		15.3	6.3	7.7
TD	24.4		23.6	11.8	22.0		34.1	18.9	21.5

The biaxially stretched microporous sheet of Example 18 was examined by scanning electron microscopy at a magnification of 430X. A section taken in a plane perpendicular to the sheet surface (viz., looking into the thickness) and along the machine direction showed substantial pore elongation. A section taken in a plane perpendicular to the sheet surface and along the transverse direction showed pore elongation which was not as pronounced as along the machine direction. A view of the sheet surface (not sectioned) showed that large void structures were not as numerous as in views of either of the sections looking into the thickness.

Tabl VII

Properties of Biaxially Stretched Microporous Sheets Produced from Precursor Sheet of Exampl 3				
Example No.	22	23	24	25
Thickness, mm	0.178	0.102	0.127	0.102
Stretch Ratio				
MD	2	2	3	3
TD	3	3	3	3
Line Speed, m/min	24.4	24.4	24.4	24.4
MDS Preheat Temp., °C	79	79	79	79
TDS Zone Temp., °C				
Preheat	177	149	177	177
Stretch I				
177-166-277	X		X	X
193-182-193		X		
Stretch II, Sinter I				
149-127-149	X		X	X
149-149-149		X		
Sinter II				
232-204-232	X		X	X
260-260-260		X		
Weight, g/m²	27	10	20	27
Porosity, vol%	90	91	90	92
Matrix Tensile Strength, MPa				
MD	29.58	52.94	77.84	109.89
TD	117.76	44.43	32.96	39.91
Elongation at Break, %				
MD	90	47	27	17
TD	9	24	32	30
Tear Strength, kN/m				
MD	15.41	10.51	15.24	7.18
TD	21.02	5.43	4.20	3.50
Gurley Air Flow, sec/100cc	56	33		36
Mullens Hydrostatic, kPa	552	655	641	586
MVTR, g/m²day	843	815	862	982
Methanol Bubble Point Pressure, kPa	303	276		317
Maximum Limiting Pore Diameter, μ m	0.074	0.081		0.070
Heat Shrinkage after 1 hr at 100°C, %				
MD	24.1	16.5	26.4	
TD	40.1	31.4	34.8	

Claims

1. A m thod for producing a microporous material by
   (a) forming a sheet from a mixture comprising
      (i) essentially linear ultrahigh molecular weight polyethylene having an intrinsic viscosity of at

least 18 deciliters/gram, or essentially linear ultrahigh molecular weight polypropylene having an intrinsic viscosity of at least 6 deciliters/gram or a mixtur thereof

(ii) finely divided particulat substantially water-insoluble siliceous filler, wherein the weight ratio of said filler to polymer being in the range of from 1:1 to 9:1 and

(iii) processing plasticizer which is liquid at room temperature and having little solvating effect on the polymer,

(b) removing said processing plasticizer from said sheet resulting in precursor microporous material having

(1) a matrix consisting of said essentially ultrahigh molecular weight polyolefin,

(2) finally divided particulate substantially water-insoluble siliceous filler distributed throughout the matrix, said filler constituting from 50 percent to 90 percent by weight of said precursor microporous material and

(3) a network of interconnecting pores communicating throughout said precursor microporous material, said pores constituting from 35 percent to 80 percent by volume of said precursor microporous material

characterized by

(c) stretching said precursor microporous material in at least one stretching direction to a stretch ratio of at least 1,5 to produce a stretched microporous material which is dimensionally stable at room temperature and comprising regions of stretched-induced molecularly orientated ultrahigh molecular weight polyolefin and wherein the network of interconnecting pores communicating throughout said stretched microporous material constituting more than 80 percent by volume of said stretched microporous material.

2. The method of claim 1
characterized by
extruding said mixture to a continuous sheet and calendering said sheet forming a continuous sheet of lesser thickness than the sheet exiting from the extrusion die.

3. The method of claim 1
characterized by
(i) substantially removing the processing plasticizer by extraction with an organic liquid which is a good solvent for the processing plasticizer, a poor solvent for the polymer and more volatile than the processing plasticizer,
(ii) substantially removing the organic extraction liquid by steam and/or water, and
(iii) drying the precursor microporous material prior stretching to remove the residual water and remaining residual organic extraction liquid.

4. The method of claim 1
characterized by
using an ultrahigh molecular weight polyethylene having an intrinsic viscosity in the range of from 18 to 39 deciliters/gram.

5. The method of claim 1
characterized in that
said filler constituting from 50 percent to 85 percent by weight of said microporous material.

6. The method of claim 1
characterized by
using silica as filler.

7. The method of claim 6
characterized in that
the filler is precipitated silica.

8. The method of claim 7
characterized in that
said precipitated silica has an average ultimate particle size of less than 0,1 µm.

9. The method of claim 1
characterized in that
th volume average diameter of said pores of said stretched microporous mat rial as determin d by mercury porosimetry is in the range from 0,6 to 50 µm.

10. The method of claim 1
characterized in that
said pores of said stretched microporous material constituting from 85 percent to 95 percent by volume of said stretched microporous material.

11. The method of claim 1
characterized by
stretching said precursor microporous material in one direction.

12. The method of claim 1
characterized by
stretching said precursor microporous material in at least two different directions.

13. The method of claim 12
characterized by
stretching said precursor microporous material to a stretch ratio of at least 1,5 in each of said two different directions.

Patentansprüche

1. Verfahren zum Herstellen eines mikroporösen Materials durch
(a) Ausbilden einer Folie aus einer Mischung enthaltend
(i) im wesentlichen lineares Polyethylen mit ultrahohem Molekulargewicht und mit einer inneren Viskosität von mindestens 18 Deciliter/Gramm, oder im wesentlichen lineares Polypropylen mit ultrahohem Molekulargewicht und einer inneren Viskosität von mindestens 6 Deciliter/Gramm, oder einer Mischung derselben,
(ii) feinteiligen teilchenförmigen, im wesentlichen wasserunlöslichen Silicatfüllstoff, wobei das Gewichtsverhältnis des Füllstoffes zu Polymer im Bereich von 1:1 bis 9:1 liegt, und
(iii) Verarbeitungsweichmacher, der bei Raumtemperatur flüssig ist und das Polymer wenig anlöst,
(b) Entfernen des Verarbeitungsweichmachers aus der Folie, so daß ein Vorläufer des mikroporösen Materials erhalten wird, mit
(1) einer Matrix, die im wesentlichen aus dem Polyolefin mit ultrahochem Molekulargewicht besteht,
(2) feinteiligem teilchenförmigen, im wesentlichen wasserunlöslichen Silikatfüllstoff, der in der Matrix verteilt ist, wobei der Füllstoff von 50 Gew% bis 90 Gew% des Vorläufers des mikroporösen Materials ausmacht, und
(3) einem Netzwerk von untereinander verbundenen Poren, die durch den Vorläufer des mikroporösen Materials kommunizieren, wobei die Poren von 35 Vol% bis 80 Vol% des Vorläufers des mikroporösen Materials ausmachen,
gekennzeichnet durch
(c) Recken des Vorläufers des mikroporösen Materials in mindestens einer Reckrichtung bis zu einem Streckverhältnis von mindestens 1,5, um ein bei Raumtemperatur dimensionsstabiles gerecktes mikroporöses Material auszubilden, das Bereiche von durch Recken erzeugten molekularausgerichtetem Polyolefin mit utrahohem Molekulargewicht enthält, wobei das Netzwerk von untereinander verbundenen Poren, die durch das gereckte mikroporöse Material kommunizieren, mehr als 80 Vol% des gereckten mikroporösen Materials ausmacht.

2. Verfahren nach Anspruch 1,
gekennzeichnet durch
Extrudieren der Mischung zu iner endlosen Folie, Kalandrieren der Folie, um eine endlose Folie von geringerer Dicke auszubilden, als die aus der Extrusionsdüse austret nde Folie.

3. Verfahren nach Anspruch 1,
gekennzeichnet durch
(i) im wesentlichen Entfernen des Verarbeitungsweichmachers durch Extraktion mit einer organischen Flüssigkeit, die ein gutes Lösemittel für den Verarbeitungsweichmacher und ein schlechtes Lösemittel für das Polymer und stärker flüchtig als der Verarbeitungsweichmacher ist,
(ii) im wesentlichen Entfernen der organischen Extraktionsflüssigkeit durch Dampf und/oder Wasser, und
(iii) Trocknen des Vorläufers des mikroporösen Materials vor dem Recken, um das restliche Wasser und den verbliebenen Rest der organischen Extraktionsflüssigkeit zu entfernen.

4. Verfahren nach Anspruch 1,
gekennzeichnet durch
Verwenden eines Polyethylens mit ultrahohem Molekulargewicht, das eine innere Viskosität im Bereich von 18 - 39 Deciliter/Gramm aufweist.

5. Verfahren nach Anspruch 1,
dadurch gekennzeichnet,
daß der Füllstoff von 50 Gew% bis 85 Gew% des mikroporösen Materials ausmacht.

6. Verfahren nach Anspruch 1,
gekennzeichnet durch
Verwenden von Siliziumdioxid als Füllstoff.

7. Verfahren nach Anspruch 6,
dadurch gekennzeichnet,
daß der Füllstoff gefälltes Siliziumdioxid ist.

8. Verfahren nach Anspruch 7,
dadurch gekennzeichnet,
daß das gefällte Siliziumdioxid eine mittlere Höchstteilchengröße von kleiner als 0,1 µm aufweist.

9. Verfahren nach Anspruch 1,
dadurch gekennzeichnet,
daß der Volumendurchmesser der Poren des gereckten mikroporösen Materials, bestimmt durch Quecksilberporosimetrie, im Bereich von 0,6 bis 50 µm liegt.

10. Verfahren nach Anspruch 1,
dadurch gekennzeichnet,
daß die Poren des gereckten mikroporösen Materials von 85 Vol% bis 95 Vol% des gereckten mikroporösen Materials ausmachen.

11. Verfahren nach Anspruch 1,
gekennzeichnet durch
Recken des Vorläufers des mikroporösen Materials in einer Richtung.

12. Verfahren nach Anspruch 1,
gekennzeichnet durch
Recken des Vorläufers des mikroporösen Materials in mindestens zwei unterschiedlichen Richtungen.

13. Verfahren nach Anspruch 12,
gekennzeichnet durch
Recken des Vorläufers des mikroporösen Materials bis zu einem Streckverhältnis von mindestens 1,5 in jeder der 2 unterschiedlichen Richtungen.

Revendications

1. Procédé de préparation d'un matériau microporeux consistant à
(a) former une feuill à partir d'un mélang comprenant

(i) un polyéthylèn à poids moléculair ultra-élevé, essentiellement linéaire ayant un viscosité intrinsèque d'au moins 18 décilitres/gramme, ou un polypropylène à poids moléculaire ultra-él vé essenti llement linéaire ayant un viscosité intrinsèque d'au moins 6 décilitres/gramme ou un mélange de ceux-ci,

(ii) une charge siliceuse pratiquement insoluble dans l'eau de particules finement divisée, la proportion pondérale de ladite charge par rapport au polymère étant comprise dans la gamme allant de 1/1 à 9/1, et

(iii) un plastifiant de fabrication qui est liquide à la température ambiante et ayant peu d'effet de solvatation sur le polymère,

(b) retirer ledit plastifiant de fabrication de ladite feuille donnant un matériau microporeux précurseur ayant

(1) une matrice constituée de ladite polyoléfine à poids moléculaire ultra-élevé essentiellement linéaire,

(2) une charge siliceuse pratiquement insoluble dans l'eau de particules finement divisées réparties à travers la matrice, ladite charge constituant de 50% à 90% en poids dudit matériau microporeux précurseur et

(3) un réseau de pores interconnectés communiquant à travers ledit matériau microporeux précurseur, lesdits pores constituant de 35% à 80% en volume dudit matériau microporeux précurseur

caractérisé par

c) l'étirage dudit matériau microporeux précurseur selon au moins une direction d'étirage à un rapport d'étirage d'au moins 1,5 pour produire un matériau microporeux étiré qui est stable en dimension à la température ambiante et qui comprend des régions de polyoléfines à poids moléculaire ultra-élevé à orientation moléculaire induite par l'étirage et où le réseau de pores interconnectés communiquant à travers ledit matériau microporeux étiré constitue plus de 80% en volume dudit matériau microporeux étiré.

2. Procédé selon la revendication 1, caractérisé par l'extrusion dudit mélange en une feuille continue et par le calendrage ladite feuille formant une feuille continue d'épaisseur inférieure à la feuille sortant de la filière d'extrusion.

3. Procédé selon la revendication 1, caractérisé par,

(i) l'élimination pratiquement complète du plastifiant de fabrication au moyen d'une extraction avec un liquide organique qui est un bon solvant du plastifiant de fabrication, un solvant médiocre pour le polymère et qui est plus volatile que le plastifiant de fabrication.

(ii) l'élimination pratiquement complète du liquide d'extraction organique par la vapeur d'eau et/ou l'eau, et

(iii) le séchage du matériau microporeux précurseur avant étirage pour éliminer l'eau résiduelle et le liquide d'extraction organique résiduel restant.

4. Procédé selon la revendication 1, caractérisé par l'utilisation d'un polyéthylène à poids moléculaire ultra-élevé ayant une viscosité intrinsèque dans la gamme de 18 à 39 décilitres/gramme.

5. Procédé selon la revendication 1, caractérisé en ce que ladite charge constitue de 50 pourcent à 85 pourcent en poids dudit matériau microporeux.

6. Procédé selon la revendication 1, caractérisé par l'utilisation de silice comme charge.

7. Procédé selon la revendication 6, caractérisé en ce que la charge est une silice précipitée.

8. Procédé selon la revendication 7, caractérisé en ce que ladite silice précipitée possède une granulométrie finale moyenne inférieure à 0,1 µm.

9. Procédé selon la revendication 1, caractérisé en ce que le diamètre moyen des volumes desdits pores dudit matériau microporeux étiré déterminé par porosimétrie au m rcure est dans la gamm allant de 0,6 à 50 µm.

10. Procédé selon la r vendication 1, caractérisé n ce que lesdits por s dudit matériau microporeux étiré

constitue de 85 pourcent à 95 pourcent en volume dudit matériau microporeux étiré.

11. Procédé selon la revendication 1, caractérisé par l'étirag dudit matériau microporeux précurseur dans une direction.

12. Procédé selon la revendication 1, caractérisé par l'étirage dudit matériau microporeux précurseur dans au moins deux directions différentes.

13. Procédé selon la revendication 12, caractérisé par l'étirage dudit matériau microporeux précurseur en une proportion d'étirage d'au moins 1,5 dans chacune desdites deux directions différentes.